

# Hydrogen Fuel Quality for FCVs

current status of efforts at CGA

THE LINDE GROUP

*Linde*

## General Update



- H5 is a bulk hydrogen installation guideline document . We are now updating H-5 with “use specific specifications” this mirrors the way NFPA-2 is being set up
- H-5 technical committee is looking for new members from outside of CGA as we make CGA H-5 into an American National Standard
- New HYCO committee started to develop operation and installation standards for SMR systems
- CGA HMCC committee chair has set up CGA AD-Hoc committees to provide input to NFPA-2, 52, & 55. The focus of ADHOC committees are now moving towards 52 and 55 proposals coming out of the NFPA 2 work and focused on 55 due November 2010 and 52 due in May 2011
- CGA , EIGA and JIGA are working with IOMA to harmonize a number of standards
- G-5.3 (hydrogen commodity specification) is going to be updated to have a FCV grade

Note that this is a draft copy for comments and not for public release

## Add definition of Motor Fuel Hydrogen (FCV grade) to CGA 5.3



### Key indicator species at the nozzle

- 100 ppm or less total non hydrogen (see note on Helium)
- Oxygen: 5 ppm or less
- Water: 5 ppm or less
- CO: 100 ppb or less

### Custody Transfer - H<sub>2</sub> supply to the station

- Grade 4.5 (any CGA Grade LH<sub>2</sub> , Grade F or L Compressed H<sub>2</sub>)

### Periodic station testing

- for trace toxics: H<sub>2</sub>S, NH<sub>3</sub>, total sulfur, etc.
- Particle contamination at the nozzle

# Modify Table 1



**Table 1—Directory of limiting characteristics:  
(Units in ppm [v/v] unless otherwise stated)**

Limiting characteristics	QVLs			
	Maxima for Type I (gaseous) hydrogen			
	B <sup>1)</sup>	D	F <sup>1)</sup>	L
Hydrogen min. %	99.95	99.99	99.995	99.999
Argon				
Carbon dioxide	10	0.5		2
Carbon monoxide	10	1		
Helium				
Nitrogen	400	25	2	2
Oxygen	10	5	1	1
Para content min. %				
Permanent particulates				<sup>3)</sup>
Total hydrocarbon content (as methane)	10	5	0.5	1
Water	34	3.5	1.5	3.5
Dew point °F	-60	<u>-91</u>	<u>-101</u>	<u>-91</u>
°C	-51.1	<u>-68.3</u>	<u>-73.9</u>	<u>-68.3</u>

<sup>1)</sup> If hydrogen is produced by mercury brine cell, then analysis for mercury vapor is required.  
<sup>2)</sup> Can include up to 50 ppm neon plus helium.  
<sup>3)</sup> To be determined between supplier and user.  
<sup>4)</sup> Includes water.

Add new table column

(Grade) FCV  
 99.97  
 (Ar): note 5  
 (CO<sub>2</sub>): 2 ppm  
 (CO): 0.1 ppm  
 (He): 300  
 (N<sub>2</sub>): note 5  
 (O<sub>2</sub>): 5 ppm  
 (Particles): 1 mg/kg (H<sub>2</sub>)  
 (THC): 2 ppm  
 (Water): 5 ppm - 85F, -65 C

Limiting characteristics  
 (as stated)

Limiting characteristics	QVLs		
	Maxima for Type II (liquid) hydrogen		
	A	C	B
Hydrogen min. %	99.995 <sup>2)</sup>	99.999	99.9997 <sup>2)</sup>
Argon	1		1
Carbon dioxide	1	2	
Carbon monoxide	39		
Helium		2	2
Nitrogen	1	1	1
Oxygen	95		95
Permanent particulates	Filtering req See 5.11	<sup>3)</sup>	
Total hydrocarbon content (as methane)	1 <sup>4)</sup>	1	
Water		3.5	
Dew point °F		<u>-91</u>	
°C		<u>-68.3</u>	

Filtering is required.

# Impurity Limits : SAE J-2719 as compared to commercial practice

THE LINDE GROUP



Constituent	Chemical Formula	Limits (ppm)	Linde-EU Grade 5.0*	CGA G-4.3 Grade 4.5
Total non hydrogen components	Grade 99.97	300	<50*	<50
Total non-hydrogen, non-helium	Grade 99.99	100	<10	<10
Water	H <sub>2</sub> O	5	<5	<5
Total Hydrocarbons	CH <sub>4</sub> , C <sub>x</sub> H <sub>y</sub>	2	<1	<1
Oxygen	O <sub>2</sub>	5	<2	<2
Helium (*not included in assay)	He	300	<50*	<50
Inerts ( Nitrogen and Argon)	N <sub>2</sub> + Ar	100	<10	<10
Carbon Dioxide	CO <sub>2</sub>	1	<1	<1
Carbon Monoxide	CO	0.1	ND/ <0.1	ND/ <0.1
Total Sulfur	Includes: H <sub>2</sub> S, COS, CS <sub>2</sub>	0.001	ND / <0.001	ND / <0.001
Formic Acid	CHOOH	0.2	ND/ <0.1	ND/ <0.1
Ammonia	NH <sub>3</sub>	0.1	ND/ <0.1	ND/ <0.1

Note that this is a draft copy for comments and not for public release

# Hydrogen Custody Transfer and Key species standard at the dispenser



**Commercial standards for motor fuel H2 are most likely satisfied when the Grade 4.5 or Grade 5 is supplied to the station. the following are suitable minimum standard at the dispenser :**

- 100 ppm or less total non hydrogen (\*disregard any helium)
- Oxygen: 5 ppm or less
- Water: 5 ppm or less
- CO: 100 ppb or less

**Commercial standards for H2 delivered to the fueling station (bulk delivery, on-site generation, on-site purifier off H2 pipeline) are generally Grade 5.0 in Europe or Grade 4.5 in USA.**

**With Grade 5.0Euro or Grade 4.5USA, the total non-H2 is < 10 ppm and toxic impurities are well below SAE J-2719 guidelines (TIR) based on initial certification of the source, and ISO grade process controls. IE .. certs are needed for only the four components noted above**

**In the fueling station system there is opportunity for the station equipment or faulty station maintenance procedures to contaminate the incoming H2 and deliver**

# Hydrogen Quality for Fuel Cell Vehicles



**SAE J-2719 and ISO/PDTS 14687-2 define the minimum purity level of fuel cell grade hydrogen as 99.99% (99.97% if we consider Helium)**

	<b>Total % hydrogen</b>	<b>Total impurities (ppmv)</b>	<b>Total impurities (ppb)</b>
<b>Grade 3</b>	<b>99.9 %</b>	<b>1000</b>	<b>1,000,000</b>
<b>Grade 4</b>	<b>99.99 %</b>	<b>100</b>	<b>100,000</b>
<b>Grade 5</b>	<b>99.999 %</b>	<b>10</b>	<b>10,000</b>
<b>Grade 6</b>	<b>99.9999 %</b>	<b>1</b>	<b>1000</b>

Note that this is a draft copy for comments and not for public release

### **As an industry we are OK if we ignore helium as a contaminant in motor fuel hydrogen....**

- FCV providers have verified that up to the agreed limit of 300 ppm Helium in motor fuel hydrogen is OK for the fuel cell system.
- Helium is difficult to distinguish from hydrogen in many analytical methods, looking for helium and accounting for helium in the assay adds cost and provides no benefit
- When special analytical methods are used, helium can be seen in some hydrogen that has been produced using natural gas that contains high levels of helium.
- no hydrogen supply system has been has ever been seen to have over 100 ppm helium in hydrogen.

### **all infrastructure providers are in agreement that helium is of no concern in hydrogen for motor fuel applications with the following exception:**

- When used to purge hydrogen compression storage and dispensing systems prior to operation, all helium should be effectively purged from the system prior to fueling vehicles.

100 ppm total non-helium impurities meets the hurdle rate for accuracy gravimetric and volumetric dispenser metrology



With commercial sales by the kilogram, we need to manage the effect of fuel composition on gas density at the dispenser so that we can limit the difference between mvol/vol and mg/kg measurement and set a fixed minimum grams of H2 per KG of motor fuel H2 sold

possible gas mixture that meets simple definition for H2 motor fuel and meets SAE 2719 and has high argon (worst case)		<b>MW Molecular Weight</b>	<b>mVol / Vol</b>	<b>mg / kg</b>	<b>nomal L / Nm3</b>	<b>grams / liter</b>	<b>mass grams/ Nm3</b>	<b>weigh %</b>
Total			<b>1,000,000</b>	<b>1,000,000</b>	1,000.00		85.37	100.00%
hydrogen	H2	2.016	<b>999,700</b>	<b>997,747</b>	999.70	0.085206	85.18	99.7747%
Helium	He	4.003	<b>200</b>	<b>396</b>	0.200	0.1691583	0.03383	0.0396%
Total non hydrogen (except He)			<b>100</b>	<b>1857</b>	0.100		0.15854	0.1857%
Nitrogen	N2	28.013	<b>5</b>	<b>69</b>	0.005	1.185293	0.00593	0.0069%
Argon	Ar	39.948	<b>80.718</b>	<b>1599</b>	0.081	1.690824	0.13648	0.1599%
water	H2O	18.015	<b>5</b>	<b>45</b>	0.005	0.764629	0.00382	0.0045%
Oxygen	O2	31.999	<b>5</b>	<b>79</b>	0.005	1.354452	0.00677	0.0079%
total Hydrocarbon as methane	CH4	16.043	<b>2</b>	<b>16</b>	0.002	0.679896	0.00136	0.0016%
Carbon Dioxide	CO2	44.010	<b>2</b>	<b>44</b>	0.002	1.871497	0.00374	0.0044%
Carbon Monoxide	CO	28.011	<b>0.2</b>	<b>3</b>	0.0002	1.185321	0.00024	0.0003%
Total Haloginates (Cl, Br,)	as Cl	70.906	<b>0.05</b>	<b>2</b>	0.0001	3.037175	0.00015	0.0002%
Formaldehyde	HCHO	30.027	<b>0.01</b>	<b>0.1</b>	0.00001	1.274424	0.00001	0.00001%
Formic acid	HCOOH	46.026	<b>0.01</b>	<b>0.2</b>	0.00001	1.953490	0.00002	0.00002%
Ammonia	NH3	17.031	<b>0.01</b>	<b>0.1</b>	0.00001	0.726017	0.00001	0.00001%
Total Sulfur (as H2S)	H2S	34.082	<b>0.002</b>	<b>0.03</b>	0.000002	1.453032	0.000003	0.000003%

Note that this is a draft copy for comments and not for public release

# Trace Fuel Cell Toxins

we don't see this stuff easily or often, but we know it is bad



—The trace impurities (shown below) that may be in hydrogen and are known to be toxic to fuel cells are not easy to measure or monitor in the field.

— laboratory analysis of these constituents is possible but pricy using new standard ASTM test methods (\*CO is measurable at these levels)

Constituent	Chemical Formula	Fuel Cell Grade (ppm)
Carbon Monoxide*	CO	0.1
Total Sulfur	Includes: H <sub>2</sub> S, COS, CS <sub>2</sub>	0.004
Formic Acid	CHOOH	0.2
Ammonia	NH <sub>3</sub>	0.1
Total Halogenates	Includes: HBr, Cl <sub>2</sub> , HCL,	0.05

Note that this is a draft copy for comments and not for public release

## way to step forward...



**We will update CGA 4.3 with the specifications for fuel cell grade hydrogen:**

### **Key species limits at the dispenser nozzle;**

- 100 ppm or less total non hydrogen (typical is less than 10 ppm)
- Oxygen: 5 ppm or less (typical is 1-3 ppm)
- Water: 5 ppm or less (typical is 1-3 ppm)
- CO: 100 ppb or less (this is pushing our limits)

### **Include SAE TIR language and FC toxin limits on:**

- trace toxics: H<sub>2</sub>S, NH<sub>3</sub>, total sulfur, etc. as per SAE J-2719
- Leave SAE J-2719 as the source document and update the CGA standard as needed

### **Protocol for station testing:**

- Test for key species and toxics (once) at station start up dispenser certification
  - Test supply system to confirm Grade 4.5 at custody transfer point
  - Test for key species limits periodically (perhaps with annual dispenser field testing by weights and measures) **and if change of H<sub>2</sub> supply to station**
  - Test toxics again if major maintenance to station?
- Note that this is a draft copy for comments and not for public release

## Fuel Cell Vehicle (FCV) Grade

Compressed hydrogen suitable to supplied a motor fuel to electric fuel cell electric vehicles to shall conform to the QVLs shown as FCV grade in table 1 as well as Table 3A and 3B with the provision or understanding that the technical information report SAE J-2719 serves as the fuel cell grade hydrogen quality guideline document and J2719.specificaions limits for hydrogen impurities that are toxic to fuel cells may be modified between 2010 and 2020

The QVL limits shown in Table 3A are the minimum requirements that must be met by the hydrogen motor fuel supplier . In most cases compliance with table 3 A will imply compliance with the impurities listed in Table 3B. Hydrogen motor fuel dispensing stations include some sort of hydrogen supply to the station (delivered bulk LH2, Compressed hydrogen tube trailers, or on-site generation system and then onsite (at the station) compression, storage and dispensing equipment (CSD). Hydrogen supply to the motor fuel dispensing station must be better than the minimum standards shown in table 3A as some contamination of the hydrogen at the dispenser nozzle to vehicle interface with atmospheric gases, moisture, and particulates is unavoidable and must be included in the hydrogen quality assurance program as testing of hydrogen delivered to FCVs at the dispenser must meet the QVL limits shown in Table 3A and 3B.

The CSD system must be constructed of materials that do not add to the impurities in the hydrogen supplied to station CSD system. This is most notably relevant in the potential for improperly specified polymeric materials of construction to outgas sulfur compounds, or the potential for the compressor subsystem to add hydrocarbons or particulate material.

Specifications for motor fuel hydrogen sold in the United States must also comply with Department of Commerce regulations in NIST Handbook 130 Section IV. Uniform Regulations Part G. Uniform Engine Fuels, Petroleum Products, and Automotive Lubricants Regulations Section 2. Standard Fuel Specifications. Draft language to be included in NIST Handbook 130 is being developed by the DOE sponsored U.S. National Work Group (USNWG) for the Development of Commercial Hydrogen Measurement Standards and is harmonized with SAE J-2719 and the FCV grade specifications in Table 1 as well as the Tables 3A and 3B in this standard.

## PC for G-5.3



**Add new column to table 1 with “FCV” grade shown in center of table**

**Hydrogen Min:99.97**

<b>(Ar):</b>	<b>note 5</b>
<b>(CO<sub>2</sub>):</b>	<b>2 ppm</b>
<b>(CO):</b>	<b>0.1 ppm</b>
<b>(He):</b>	<b>300</b>
<b>(N<sub>2</sub>):</b>	<b>note 5</b>
<b>(O<sub>2</sub>):</b>	<b>5 ppm</b>
<b>(Particles):</b>	<b>1 mg/kg (H<sub>2</sub>)</b>
<b>(THC):</b>	<b>2 ppm</b>
<b>(Water):</b>	<b>5 ppm</b>

**Add note 5 to table 1: total of all non-hydrogen and non-helium constituents in FCV grade hydrogen shall not exceed 100 ppm**

**Add QLV for FCV grade H<sub>2</sub> to Table 2. Typical use: motor vehicle fuel for H<sub>2</sub> powered fuel cell electric vehicles.**



**unless there is a verifiable test method, dispenser quality tests are not enforceable**

**A “verified test method” is :**

- Established for at least 5 years
- Verifiable with round robin tested laboratories
- Has defined, traceable standards for impurities

**We will need a transition period from 2015 to 2020 for test method development to be established as commercial practice**

## Notes on this presentation



**This presentation is provided as a suggestion of how I believe we can simplify the approach to H2 fuel quality for motor vehicle sales to support FCVs**

**If I have circulated this to you, you may circulate within your organization and I look forward to your comments. Please do not transmit this outside your organization**

**Robert Boyd**

**Bob.boyd @ Linde.com**

**510.786.5903 (office)**

**510.415.3588**